

Generalized Kohn-Sham Density-Functional Theory via Effective Action Formalism.

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We present a rigorous formulation of generalized Kohn-Sham density-functional theory. This provides a straightforward Kohn-Sham description of many-body systems based not only on particle-density but also on any other observable. We illustrate the formalism for the case of a particle-density based description of a nonrelativistic many-electron system. We obtain a simple diagrammatic expansion of the exchange-correlation functional in terms of Kohn-Sham single-particle orbitals and energies; develop systematic Kohn-Sham formulation for one electron propagators and many-body excitation energies. This work is ideally suited for practical applications and provides a rigorous basis for a systematic development of the existing body of first-principles calculations in a controllable fashion.

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I. INTRODUCTION

Density-functional theory¹ allows one to study the ground state properties of the many-body system in terms of the expectation value of the particle-density operator. In principle, it offers the possibility of finding the ground state energy E_g by minimizing the energy functional that depends on the density only:

$$E_g = \min_n E[n]. \quad (1)$$

Similar theories can be formulated in terms of the expectation values of a spin-density operator or current-density operator, known as spin-density² and current-density functional theory.³ In general, one can imagine a description of a many-body system in terms of the expectation value of any other suitable operator. Such a general description can be elegantly presented via the effective action formalism,^{4,5} thus leading to a *generalized* density-functional theory – a theory that allows a description of many-body systems in terms of the expectation value of any suitable operator.

Proving the existence of such a theory is not a trivial matter. In fact, the conventional density-functional theory relies heavily on the theorem of Hohenberg and Kohn,¹ which shows that there exists a *unique* description of a many-body system in terms of the expectation value of the particle-density operator. Finite-temperature extension of this theorem was given by Mermin.⁶ Similar results have been obtained for spin-density and current-density-functional theory.^{2,3} Clearly, it is absolutely important to establish the corresponding existence theorems when constructing a generalized density-functional theory. In the framework of the effective action formalism, the proof of existence was given only in a diagrammatic sense and was tightly tailored to the particular features of the particle-density based description of a nonrelativistic many-electron system.⁴ In this work we present a different resolution of this important issue. Our formulation is valid for a general case and does not rely on any perturbative expansions. Not only does this offer an alternative proof of the previous results for density-, spin-density-, current-density-functional theories, but it also provides a rigorous foundation for generalized density-functional theory.

However important the formal question of existence is, it is of little help for the actual construction of the required density or other functionals. For example, to make any practical use of the conventional density-functional theory, an explicit (perhaps approximate) expression for the energy functional (1) is necessary. An important contribution here was made by Kohn and Sham.⁷ They proposed a certain decomposition of the energy functional, which for a typical nonrelativistic many-fermion system,

$$\begin{aligned} \hat{H} = & \int d\mathbf{x} \hat{\psi}^\dagger(\mathbf{x}) \left(-\frac{1}{2m} \nabla^2 + v_{ion}(\mathbf{x}) \right) \hat{\psi}(\mathbf{x}) \\ & + \frac{e^2}{2} \int \int \frac{\hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}^\dagger(\mathbf{y}) \hat{\psi}(\mathbf{y}) \hat{\psi}(\mathbf{x})}{|\mathbf{x} - \mathbf{y}|} d\mathbf{x} d\mathbf{y}, \end{aligned} \quad (2)$$

takes the form

$$E[n] = T_s[n] + \int v_{ion}(\mathbf{x})n(\mathbf{x})d\mathbf{x} + \frac{e^2}{2} \iint \frac{n(\mathbf{x})n(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}d\mathbf{x}d\mathbf{y} + E_{xc}[n]. \quad (3)$$

Here $T_s[n]$ is the kinetic energy of an auxiliary system of noninteracting fermions that yields the ground state density $n(\mathbf{x})$, and $E_{xc}[n]$ is the exchange-correlation energy. Once the approximation for $E_{xc}[n]$ has been decided, the minimization of the functional (3) leads to the familiar Kohn-Sham single-particle equations.⁸ This approach represents the so-called Kohn-Sham density-functional theory.

A natural question now arises: is there an analog of Kohn-Sham density-functional theory in the effective action formalism? In the original work of Fukuda, Kotani, Suzuki and Yokojima⁴ the relationship between the two methods was not established. Understanding the place of Kohn-Sham theory in the effective action formalism is important for a number of reasons. A vast majority of first-principles calculations are based on the Kohn-Sham method.^{9,10} The remarkable success of these calculations points to the fact that this seemingly ad hoc decomposition provides a very good approximation of the energy functional. As we show in this work, the connection between the effective action formalism and the Kohn-Sham method can be rigorously established via the inversion method.¹¹ The realization of this fact immediately leads to a generalized Kohn-Sham theory.

A distinct feature of the effective action formulation of generalized Kohn-Sham theory is that it provides a systematic way of calculating the required functionals. For example, in case of particle-density based description of nonrelativistic many-electron systems, it leads to a set of simple diagrammatic rules for constructing the exchange-correlation functional entirely in terms of Kohn-Sham derived quantities. We construct the first few orders of the exchange-correlation functional, comment on the local density approximation, and discuss our results as compared to other methods.^{9,12,13}

Applications of the presented formalism is not restricted to the exchange-correlation functional only. We have already demonstrated that this method is capable of establishing rigorous Kohn-Sham density-functional formulation of one-electron propagators.¹⁴ We briefly discuss the main results of that work and compare it with the existing strategies for construction of one-electron propagators.¹⁵⁻¹⁷ Lastly, we analyze the excitation energies within the effective action formalism and comment on the relationship with similar results^{18,19} obtained via time-dependent density-functional theory.²⁰

II. EFFECTIVE ACTION FUNCTIONAL

The effective action formalism in the context of density-functional theory was discussed by Fukuda, Kotani, Suzuki and Yokojima.⁴ Here we describe the main features of this method and prove the generalized existence theorems. We start by defining the functional $W[J]$ as,

$$e^{-\beta W[J]} = \text{Tr} \left(e^{-\beta(\hat{H} + J(1)\hat{Q}(1))} \right).$$

Here \hat{H} denotes the Hamiltonian of the system under consideration. Parameter β can be identified with inverse temperature. \hat{Q} is the operator whose expectation value will serve as a main variable of the theory, and J is the external source coupled to it. Both \hat{H} and \hat{Q} are assumed to be time-independent. Summation over repeated indexes is assumed, and the notation $J(1)\hat{Q}(1)$ embodies all the necessary summations and integrations. For example, to formulate the theory in terms of the expectation value of the particle-density operator $\hat{n}(\mathbf{x})$, we choose $\hat{Q} = \hat{n}(\mathbf{x})$ and

$$J(1)\hat{Q}(1) \equiv \int d\mathbf{x} J(\mathbf{x}) \hat{n}(\mathbf{x}).$$

Thermal expectation value of \hat{Q} ,

$$Q(1) = \frac{\text{Tr} \left(\hat{Q}(1) e^{-\beta(\hat{H} + J(1')\hat{Q}(1'))} \right)}{\text{Tr} \left(e^{-\beta(\hat{H} + J(1')\hat{Q}(1'))} \right)},$$

can be written in terms of $W[J]$ as,

$$Q(1) = \frac{\delta W[J]}{\delta J(1)}. \quad (4)$$

Denoting the set of allowable external sources as \mathcal{J} and the set of all generated expectation values of Q as \mathcal{Q} , we can establish a map $\mathcal{J} \rightarrow \mathcal{Q}$. We assume that for a given element of \mathcal{J} there corresponds only one element of \mathcal{Q} , in other words, given the external source we can unambiguously establish the expectation value that it generates. Whether the converse of this statement is true remains to be proven. The following property of the functional $W[J]$ is of fundamental importance.

Theorem 1: *The functional $W[J]$ is strictly concave, i.e. for any α , $0 < \alpha < 1$, and $J \neq J'$*

$$W[\alpha J + (1 - \alpha) J'] > \alpha W[J] + (1 - \alpha) W[J'].$$

Based on strict concavity of $W[J]$ one can prove the following result.

Corollary 1: *The map $\mathcal{J} \rightarrow \mathcal{Q}$ is one-to-one.*

The proofs of these statements are given in the appendix. Corollary 1 guarantees that the functional relationship between J and Q can be inverted:

$$\frac{\delta W[J]}{\delta J(1)} = Q(1) \Rightarrow J = J[Q]. \quad (5)$$

When $\hat{Q} = \hat{n}(\mathbf{x})$, Corollary 1 represents an alternative proof to the theorem of Mermin.⁶

The functional $W[J]$ provides a description of the physical system in terms of the external probe J . We, on the other hand, want the description in terms of Q . The change of variables from J to Q can be accomplished via a functional Legendre transformation.²¹ This leads to the definition of the effective action functional:

$$\Gamma[Q] = W[J] - J(1') Q(1'). \quad (6)$$

Here, J is assumed to be a functional of Q from Eqn (5). The functional $\Gamma[Q]$ possesses the following important property.

Proposition 1: *The effective action functional $\Gamma[Q]$ defined on the set \mathcal{Q} is strictly convex.*

Proof of this statement is given in the appendix. Differentiating (6) with respect to Q , we obtain

$$\frac{\delta \Gamma[Q]}{\delta Q(1)} = -J(1). \quad (7)$$

Since our original system is recovered when $J = 0$, we arrive at the important variational principle: the functional $\Gamma[Q]$ reaches a minimum at the exact expectation value of \hat{Q} ,

$$\left(\frac{\delta \Gamma[Q]}{\delta Q} \right)_{Q=Q_g} = 0.$$

In the zero temperature limit, $\beta \rightarrow \infty$, Q_g represents the exact ground state expectation value of \hat{Q} and $\Gamma[Q_g]$ equals the exact ground state energy. Obviously, at finite temperatures

$$\Gamma[Q_g] = -\frac{1}{\beta} \ln \text{Tr} \left(e^{-\beta \hat{H}} \right),$$

$$Q_g(1) = \frac{\text{Tr} \left(\hat{Q}(1) e^{-\beta \hat{H}} \right)}{\text{Tr} \left(e^{-\beta \hat{H}} \right)}.$$

The effective action formalism furnishes a rigorous formulation of generalized density-functional theory. The existence of $\Gamma[Q]$ is guaranteed by Corollary 1. When \hat{Q} is a particle-density operator, we obtain conventional density-functional theory; when \hat{Q} stands for a spin-density operator, we have spin-density-functional theory;² when \hat{Q} is a current operator, we obtain current-density-functional theory,³ etc.

To implement this formally exact method, an approximation of the effective action functional $\Gamma[Q]$ is required. For a particle-density based description of a nonrelativistic many-electron system the effective action functional can be approximated via the auxiliary field method.⁴ However, this method does not lead⁴ to Kohn-Sham version of density-functional theory. The relationship between the effective action formalism and Kohn-Sham density-functional theory can be established via the inversion method.¹¹

III. GENERALIZED KOHN-SHAM THEORY VIA THE INVERSION METHOD

Consider the following general Hamiltonian

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}_{int}$$

which depends on the coupling constant λ as a parameter. The same is true for the effective action functional

$$\Gamma = \Gamma [Q, \lambda].$$

Clearly Q, λ are to be considered as two independent variables. Note, however, that this does not prevent the exact expectation value Q_g from depending on λ : this dependence is fixed by the variational principle

$$\left(\frac{\delta \Gamma [Q, \lambda]}{\delta Q} \right)_{Q_g} = 0. \quad (8)$$

The functional $\Gamma [Q, \lambda]$ is defined as,

$$\Gamma [Q, \lambda] = W [J, \lambda] - J (1') Q (1'), \quad (9)$$

where J is functional of Q and λ . This functional dependence is provided by the equation

$$\frac{\delta W [J, \lambda]}{\delta J (1)} = Q (1).$$

The inversion method^{5,11} proceeds by expanding all the quantities in Eqn (9) in terms of λ ;

$$J [Q, \lambda] = J_0 [Q] + \lambda J_1 [Q] + \lambda^2 J_2 [Q] + \dots,$$

$$W [J, \lambda] = W_0 [J] + \lambda W_1 [J] + \lambda^2 W_2 [J] + \dots, \quad (10)$$

$$\Gamma [Q, \lambda] = \Gamma_0 [Q] + \lambda \Gamma_1 [Q] + \lambda^2 \Gamma_2 [Q] + \dots$$

Comparison of the two sides in Eqn (9) for different orders of λ ,

$$\begin{aligned} \sum \lambda^i \Gamma_i [Q] &= \sum \lambda^i W_i \left[\sum \lambda^k J_k [Q] \right] \\ &\quad - \sum \lambda^i J_i (1) Q (1), \end{aligned} \quad (11)$$

leads to the expression for $\Gamma_l [Q]$,

$$\begin{aligned} \Gamma_l [Q] &= W_l [J_0] + \sum_{k=1}^l \frac{\delta W_{l-k} [J_0]}{\delta J_0 (1)} J_k (1) - J_l (1) Q (1) \\ &\quad + \sum_{m=2}^l \frac{1}{m!} \sum_{k_1, \dots, k_m \geq 1}^{k_1 + \dots + k_m \leq l} \frac{\delta^m W_{l-(k_1 + \dots + k_m)} [J_0]}{\delta J_0 (1) \dots \delta J_0 (m)} \times \\ &\quad \times J_{k_1} (1) \dots J_{k_m} (m) \end{aligned}$$

Functionals $\{W_l [J_0]\}$ and its derivatives are assumed to be known; they can usually be obtained via standard many-body perturbation techniques (specific examples will be given in the next section). Since Q and λ are considered to be independent, it follows from Eqn (7) that functionals $\{J_k [Q]\}$ can be obtained using,

$$\frac{\delta \Gamma_k [Q]}{\delta Q (1)} = -J_k (1). \quad (12)$$

Consider the zeroth order term,

$$\Gamma_0 [Q] = W_0 [J_0] - J_0 (1) Q (1). \quad (13)$$

Using Eqn (12)

$$\begin{aligned} -J_0(1) &= \frac{\delta W_0[J_0]}{\delta J_0(1')} \frac{\delta J_0(1')}{\delta Q(1)} - J_0(1) - Q(1') \frac{\delta J_0(1')}{\delta Q(1)} \\ &\Rightarrow \left(\frac{\delta W_0[J_0]}{\delta J_0(1')} - Q(1') \right) \frac{\delta J_0(1')}{\delta Q(1)} = 0. \end{aligned}$$

Strict convexity of $\Gamma_0[Q]$ (see Proposition 1) prohibits $(\delta J_0(1')/\delta Q(1))$ from having zero eigenvalues. Thus we obtain that J_0 obeys the equation:

$$Q(1) = \frac{\delta W_0[J_0]}{\delta J_0(1)}. \quad (14)$$

Hence J_0 is determined as a potential which generates the expectation value Q in the *noninteracting* ($\lambda = 0$) system. Notice that the same exact notion appears in Kohn-Sham formalism.⁸ We refer to this noninteracting system as Kohn-Sham (KS) system and J_0 as Kohn-Sham potential. Eqn (14) allows one to simplify the expression for $\Gamma_l[Q]$, which now becomes,

$$\begin{aligned} \Gamma_l[Q] &= W_l[J_0] - \delta_{l,0} J_0(1) Q(1) + \sum_{k=1}^{l-1} \frac{\delta W_{l-k}[J_0]}{\delta J_0(1)} J_k(1) \\ &\quad + \sum_{m=2}^l \frac{1}{m!} \sum_{k_1, \dots, k_m \geq 1}^{k_1 + \dots + k_m \leq l} \frac{\delta^m W_{l-(k_1 + \dots + k_m)}[J_0]}{\delta J_0(1) \dots \delta J_0(m)} \times \\ &\quad \times J_{k_1}(1) \dots J_{k_m}(m). \end{aligned}$$

The important message here is that the expression for $\Gamma_l[Q]$ involves only lower order functionals ($l-1, l-2, \dots, 0$). Thus starting with J_0 we can determine $\Gamma_1[Q]$ as

$$\Gamma_1[Q] = W_1[J_0]. \quad (15)$$

From $\Gamma_1[Q]$ we can find J_1 as,

$$J_1(1) = -\frac{\delta \Gamma_1[Q]}{\delta Q(1)} = -\frac{\delta \Gamma_1[Q]}{\delta J_0(1')} \frac{\delta J_0(1')}{\delta Q(1)},$$

or

$$J_1(1) = \mathcal{D}(1,2) \frac{\delta W_1[J_0]}{\delta J_0(2)}, \quad (16)$$

where the inverse propagator is defined as,

$$\mathcal{D}(1,2) = -\frac{\delta J_0(2)}{\delta Q(1)} = -\left(\frac{\delta^2 W_0[J_0]}{\delta J_0(1) \delta J_0(2)} \right)^{-1}.$$

Once J_1 is known, we can find $\Gamma_2[Q]$:

$$\begin{aligned} \Gamma_2[Q] &= W_2[J_0] + \frac{\delta W_1[J_0]}{\delta J_0(1)} J_1(1) \\ &\quad + \frac{1}{2} \frac{\delta^2 W_0[J_0]}{\delta J_0(1) \delta J_0(2)} J_1(1) J_1(2), \end{aligned}$$

or using Eqn (16)

$$\Gamma_2[Q] = W_2[J_0] + \frac{1}{2} \frac{\delta W_1[J_0]}{\delta J_0(1)} \mathcal{D}(1,2) \frac{\delta W_1[J_0]}{\delta J_0(2)}. \quad (17)$$

From $\Gamma_2 [Q]$ the expression for J_2 follows as,

$$\begin{aligned} J_2 (1) = & \mathcal{D} (1, 2) \frac{\delta W_2 [J_0]}{\delta J_0 (2)} \\ & + \mathcal{D} (1, 2) \frac{\delta^2 W_1 [J_0]}{\delta J_0 (2) \delta J_0 (2')} J_1 (2') \\ & + \frac{1}{2} \mathcal{D} (1, 2) \frac{\delta^3 W_0 [J_0]}{\delta J_0 (2) \delta J_0 (3) \delta J_0 (4)} J_1 (3) J_1 (4). \end{aligned} \quad (18)$$

This, in turn, leads to $\Gamma_3 [Q]$ and so on. In this hierarchical fashion one can consistently determine $\Gamma [Q, \lambda]$ to any required order;

$$\Gamma_0 \rightarrow J_0 \rightarrow \Gamma_1 \rightarrow J_1 \rightarrow \Gamma_2 \rightarrow J_2 \rightarrow \dots$$

The important point here is that all higher orders are completely determined by the Kohn-Sham potential J_0 . Let us now apply the variational principle to our expansion of $\Gamma [Q, \lambda]$:

$$\frac{\delta \Gamma [Q, \lambda]}{\delta Q (1)} = 0.$$

Since

$$\frac{\delta \Gamma_0 [Q]}{\delta Q (1)} = -J_0 (1),$$

we have the following important result

$$J_0 (1) = \frac{\delta \Gamma_{int} [Q]}{\delta Q (1)} = -\mathcal{D} (1, 1') \frac{\delta \Gamma_{int} [Q]}{\delta J_0 (1')}, \quad (19)$$

where

$$\Gamma_{int} [Q] = \sum_{i=1} \lambda^i \Gamma_i [Q].$$

Since at any order the effective action functional is completely determined by Kohn-Sham potential J_0 , we arrive at generalized Kohn-Sham self-consistent method:

1. Choose the approximation for $\Gamma_{int} [Q]$ (one obvious choice is to truncate the expansion at some order).
2. Start with some reasonable guess for the Kohn-Sham potential J_0 .
3. Calculate $\Gamma_{int} [Q]$.
4. Determine new Kohn-Sham potential J_0 via Eqn (19).
5. Repeat from step 3 until self-consistency is achieved.

The formalism described above can be applied to any general case and provides a rigorous basis for generalized Kohn-Sham theory. Practical implementation of the self-consistent procedure obviously depends on the particular Hamiltonian under consideration and the choice of the operator \hat{Q} . In the next section we apply this method to the case of a particle-density based description of nonrelativistic many-electron system.

IV. KOHN-SHAM DENSITY-FUNCTIONAL THEORY.

A. Derivation of Kohn-Sham decomposition

Let us consider a typical nonrelativistic many-electron system described by the Hamiltonian (2) and develop the description in terms of the particle-density operator:

$$\hat{Q}(1) = \hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x}) \equiv \hat{n}(\mathbf{x}).$$

For convenience, the spin degrees of freedom are suppressed here (those can be easily recovered if necessary). The role of the coupling constant λ is played by e^2 . We now evaluate the effective action functional $\Gamma[n]$ using the inversion method¹¹ described in the previous section. Coupling constant expansion of the functional $W[J_0, e^2]$,

$$W[J_0, e^2] = W_0[J_0] + e^2 W_1[J_0] + e^4 W_2[J_0] + \dots,$$

can be conveniently generated using path integral representation²³

$$e^{-\beta W[J]} = \int D\psi^\dagger D\psi e^{-S[\psi^\dagger, \psi] - \int J(\mathbf{x})\psi^\dagger(x)\psi(x)dx}. \quad (20)$$

Here

$$\begin{aligned} S[\psi^\dagger, \psi] &= \int dx \psi^\dagger(x) \left[\frac{\partial}{\partial \tau} - \frac{\nabla^2}{2m} + v_{ion}(\mathbf{x}) \right] \psi(x) \\ &+ \frac{e^2}{2} \int \int dx dx' \psi^\dagger(x) \psi^\dagger(x') u(x - x') \psi(x') \psi(x), \end{aligned} \quad (21)$$

$$u(x - x') = \frac{\delta(\tau - \tau')}{|\mathbf{x} - \mathbf{x}'|},$$

$$\int dx \equiv \int_0^\beta d\tau \int d\mathbf{x}.$$

and ψ^\dagger, ψ denote Grassmann fields.²³

The zeroth order term is given by,

$$W_0[J_0] = -\frac{1}{\beta} \sum_i \ln(1 + e^{-\beta \varepsilon_i}),$$

where ε_i 's denote single-particle energies of Kohn-Sham noninteracting system:

$$\left(-\frac{\nabla^2}{2m} + v_{ion}(\mathbf{x}) + J_0(\mathbf{x}) \right) \varphi_i(\mathbf{x}) = \varepsilon_i \varphi_i(\mathbf{x}),$$

$$n(\mathbf{x}) = \sum_i n_i |\varphi_i(\mathbf{x})|^2, \quad n_i = (e^{\beta \varepsilon_i} + 1)^{-1}.$$

First order term is given by,

$$W_1[J_0] = \frac{1}{2\beta} \text{ (diagram: two circles connected by a dotted line)} - \frac{1}{2\beta} \text{ (diagram: a circle with a vertical dotted line)} \quad (22)$$

Here solid lines denote Matsubara Green's function of Kohn-Sham noninteracting system

$$\mathcal{G}_0(\mathbf{x}\tau, \mathbf{x}'\tau') = \begin{cases} \tau > \tau', \sum \varphi_i(\mathbf{x}) \varphi_i^*(\mathbf{x}') e^{-\varepsilon_i(\tau - \tau')} (n_i - 1) \\ \tau \leq \tau', \sum \varphi_i(\mathbf{x}) \varphi_i^*(\mathbf{x}') e^{-\varepsilon_i(\tau - \tau')} n_i \end{cases}$$

and dotted line stands for the Coulomb interaction $u(x - x')$. The explicit expression for $W_1[J_0]$ is given by,

$$\begin{aligned} W_1[J_0] &= \frac{1}{2\beta} \int \int \mathcal{G}_0(x, x) u(x - x') \mathcal{G}_0(x', x') dx dx' \\ &- \frac{1}{2\beta} \int \int \mathcal{G}_0(x, x') u(x - x') \mathcal{G}_0(x', x) dx dx'. \end{aligned} \quad (23)$$

The second order term is

$$W_2[J_0] = \frac{1}{4\beta} \text{diagram 1} - \frac{1}{4\beta} \text{diagram 2} \quad (24)$$

$$+ \frac{1}{2\beta} \text{diagram 3} - \frac{1}{\beta} \text{diagram 4} \quad (25)$$

$$+ \frac{1}{2\beta} \text{diagram 5} \quad (26)$$

Similarly, one can generate higher order terms. Let us now calculate the first few orders of the effective action functional. Using Eqn (13), the zeroth order correction is given by,

$$\Gamma_0[n] = -\frac{1}{\beta} \sum_i \ln(1 + e^{-\beta \varepsilon_i}) - \int J_0(\mathbf{x}) n(\mathbf{x}) d\mathbf{x}.$$

In the zero temperature limit, $\beta \rightarrow \infty$, this transforms to

$$\Gamma_0[n] = \sum_{i=1}^N \varepsilon_i - \int J_0(\mathbf{x}) n(\mathbf{x}) d\mathbf{x},$$

or

$$\Gamma_0[n] = T_0[n] + \int v_{ion}(\mathbf{x}) n(\mathbf{x}) d\mathbf{x}.$$

Hence at zeroth order, the effective action functional is given by the sum of kinetic energy $T_0[n]$ and ion-potential energy of the *Kohn-Sham noninteracting system*. From Eqn (15), the first order correction is given by,

$$\Gamma_1[n] = W_1[J_0].$$

The expression for $W_1[J_0]$ has been presented earlier (see Eqn (22)). In the zero temperature limit

$$\begin{aligned} \Gamma_1[n] = & \frac{1}{2} \int \int \frac{n(\mathbf{x}) n(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d\mathbf{x} d\mathbf{x}' \\ & - \frac{1}{2} \int \int \frac{n(\mathbf{x}, \mathbf{x}') n(\mathbf{x}', \mathbf{x})}{|\mathbf{x} - \mathbf{x}'|} d\mathbf{x} d\mathbf{x}', \end{aligned}$$

where $n(\mathbf{x}, \mathbf{x}') = \sum \varphi_i(\mathbf{x}) \varphi_i^*(\mathbf{x}')$. Here, the first term represents the classical Hartree energy and the second term represents the exchange energy. Both are evaluated with respect to Kohn-Sham noninteracting system.

Postponing the evaluation of the second order term until the next section, let us summarize the results we have obtained. It is clear that in the zero temperature limit the expansion for the effective action functional,

$$\begin{aligned} \Gamma[n] = & T_0[n] + \int v_{ion}(\mathbf{x}) n(\mathbf{x}) d\mathbf{x} \\ & + \frac{e^2}{2} \int \int \frac{n(\mathbf{x}) n(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d\mathbf{x} d\mathbf{x}' \\ & - \frac{e^2}{2} \int \int \frac{n(\mathbf{x}, \mathbf{x}') n(\mathbf{x}', \mathbf{x})}{|\mathbf{x} - \mathbf{x}'|} d\mathbf{x} d\mathbf{x}' \\ & + \sum_{i=2} e^{2i} \Gamma_i[n], \end{aligned} \quad (27)$$

coincides with the decomposition proposed by Kohn and Sham.⁷ Therefore the inversion method of evaluating the effective action functional¹¹ naturally leads to the Kohn-Sham density-functional theory. Application of the variational principle (see Eqn (8)) to the expansion (27) yields the well-known Kohn-Sham self-consistent procedure and the corresponding single-particle equations. Comparison of Eqns (3) and (27) immediately provides an expression for the exchange-correlation functional. These topics are discussed in detail in the following sections.

To conclude this section, we would like to note that alternatively, the effective action functional can be also evaluated via the auxiliary field method⁴ However, in this method the Kohn-Sham decomposition has to be artificially imposed to allow the study of the exchange-correlation functional²² or Kohn-Sham density-functional theory in general.

B. Construction of the exchange-correlation functional

The success of first-principles calculations based on Kohn-Sham density-functional theory depends on the accuracy of the approximations to the exchange-correlation functional. The analysis of Kohn-Sham theory, or E_{xc} in particular, via standard many-body perturbation theory^{9,10} was always a challenging task, for there was no explicit connection between the two methods. The advantage of the effective action formalism is that it is a rigorous many-body approach specifically designed for a density-based description of many-body systems. This formalism provides a natural definition of the exchange-correlation functional as,

$$E_{xc}[n] = -\frac{1}{2\beta} \text{ (diagram: a circle with a vertical dashed line through the center and an arrow pointing clockwise)} + \sum_{i=2} e^{2i} \Gamma_i[n].$$

This expression involves only Kohn-Sham based quantities and is especially suitable for practical applications. Simple diagrammatic rules for evaluating higher order terms in the expansion of $\Gamma[n]$ are readily available.^{5,11} This, in turn leads to the following set of rules for the calculation of the exchange-correlation functional:

1. Draw all connected diagrams made of Kohn-Sham propagators $\mathcal{G}_0(x, x')$ and Coulomb interaction lines $u(x - x')$ with the corresponding weight factors.²³
2. Eliminate all the graphs that can be separated by cutting a single Coulomb interaction line.
3. For each two-particle reducible (2PR) graph (i.e. any graph that can be separated by cutting two propagator lines) perform the following procedure.⁵
 - (a) Separate the graph by cutting 2PR propagators.
 - (b) For each of the two resulting graphs join two external propagators.
 - (c) Connect the two graphs via the inverse density propagator $\mathcal{D}(\mathbf{x}, \mathbf{x}')$.
 - (d) Repeat the procedure until no new graph is produced.
 - (e) Sum up all the resulting graphs including the original graph.

The inverse density propagator $\mathcal{D}(\mathbf{x}, \mathbf{x}')$ is given by,

$$\mathcal{D}(\mathbf{x}, \mathbf{x}') = - \left[\int_0^\beta \mathcal{G}_0(\mathbf{x}\tau, \mathbf{x}'\tau') \mathcal{G}_0(\mathbf{x}'\tau', \mathbf{x}\tau) d\tau' \right]^{-1},$$

or in terms of Kohn-Sham orbitals

$$\mathcal{D}(\mathbf{x}, \mathbf{x}') = - \left[\sum_{i \neq j} (n_i - n_j) \frac{\varphi_i(\mathbf{x}) \varphi_i^*(\mathbf{x}') \varphi_j(\mathbf{x}') \varphi_j^*(\mathbf{x})}{\varepsilon_i - \varepsilon_j} \right]^{-1}. \quad (28)$$

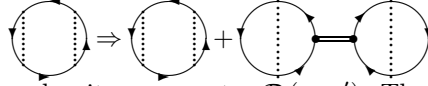
Application of these rules for generation of the first-order correction to $E_{xc}[n]$ is obvious and leads to the well-known Kohn-Sham exchange functional:^{12,13,22,24}

$$E_{xc,1} = -\frac{1}{2\beta} \text{ (diagram: a circle with a vertical dashed line through the center and an arrow pointing clockwise)}$$

Let us now consider the second order correction to $E_{xc}[n]$. Rule # 1 leads to the already given expression for $W_2[J_0]$ (see Eqn (26)). Application of Rule # 2 leads to elimination of the last two graphs, thus giving

$$\frac{1}{4\beta} \text{ (diagram: a circle with two dashed lines crossing at the center and an arrow pointing clockwise)} - \frac{1}{4\beta} \text{ (diagram: two circles connected by two horizontal dashed lines)} + \frac{1}{2\beta} \text{ (diagram: a circle with a vertical dashed line through the center and an arrow pointing clockwise)}$$

The third graph in the above expression is 2PR. According to Rule # 3 it transforms to:



Here double solid line denotes the inverse density propagator $\mathcal{D}(\mathbf{x}, \mathbf{x}')$. Therefore the final expression for the second order correction to E_{xc} is given by,

$$E_{xc,2} = \frac{1}{4\beta} \text{[Diagram: circle with two dashed lines crossing]} - \frac{1}{4\beta} \text{[Diagram: two circles connected by two dashed lines]} + \frac{1}{2\beta} \text{[Diagram: circle with a vertical dashed line]} + \frac{1}{2\beta} \text{[Diagram: two circles connected by a double solid line, each with a vertical dashed line]}$$

It is instructive to apply the above procedure to the case of a homogeneous electron gas in the zero temperature limit. It can be demonstrated that in this case Rule #3 leads to the complete elimination of 2PR graphs. Indeed, at this limit one can show that

$$\text{[Diagram: circle with a black dot and a vertical dashed line]} + \text{[Diagram: two circles connected by a double solid line, each with a black dot and a vertical dashed line]} = 0.$$

Here, black circles denote parts of the diagram that are connected to each other via two propagators. For example, in the expression for the second order correction to E_{xc} the last two graphs completely cancel each other

$$\text{[Diagram: circle with a vertical dashed line]} + \text{[Diagram: two circles connected by a double solid line, each with a vertical dashed line]} = 0,$$

and as expected,⁹

$$E_{xc,2}^{\text{hom}} = \frac{1}{4\beta} \text{[Diagram: circle with two dashed lines crossing]} - \frac{1}{4\beta} \text{[Diagram: two circles connected by two dashed lines]}$$

Local Density Approximation (LDA) represents a popular choice for $E_{xc}[n]$ in first-principles calculations. This approximation and subsequent corrections can be obtained via the derivative expansion²⁶ of the exchange-correlation functional

$$E_{xc}[n] = \int \left(E_{xc}^{(0)}(n(\mathbf{x})) + E_{xc}^{(2)}(n(\mathbf{x})) (\nabla n(\mathbf{x}))^2 + \dots \right) d\mathbf{x}$$

where $E_{xc}^{(k)}$ is a *function* of $n(\mathbf{x})$, not a functional.

LDA corresponds to the first term in this expansion;

$$E_{xc}^{\text{LDA}}[n] \equiv \int E_{xc}^{(0)}(n(\mathbf{x})) d\mathbf{x}.$$

Function $E_{xc}^{(0)}(n(\mathbf{x}))$ can be found by evaluating the above expansion at constant density $n(\mathbf{x}) = n_0$

$$E_{xc}^{(0)}(n_0) = \frac{1}{V} E_{xc}[n_0], \quad n_0 = \text{const.}$$

Here $E_{xc}[n_0]$ represents the exchange-correlation energy of the homogeneous electron gas with density n_0 .

Regarding the results obtained in this section, we would like to emphasize the following points. Not only does the effective action formalism leads to a straightforward set of rules to calculate the exchange-correlation functional up to any arbitrary order, but it can also be used to generate similar quantities for descriptions based on the observables other than particle density (for example, current-density functional theory). One should also remember that the expansion of $E_{xc}[n]$ represents only part of the general picture provided by the effective action formalism. As we show later, the same formalism allows us to develop a rigorous and systematic Kohn-Sham theory for one-electron propagators and many-body excitation energies.

C. Kohn-Sham self-consistent procedure

As we have demonstrated earlier, application of the variational principle leads to the Kohn-Sham self-consistent procedure. In the case of the traditional density-functional theory, the typical self-consistent procedure takes the form

1. Start with some reasonable guess for the Kohn-Sham potential $J_0(\mathbf{x})$.
2. Solve Kohn-Sham single-particle equations.
3. Determine new Kohn-Sham potential $J_0(\mathbf{x})$ using

$$J_0(\mathbf{x}) = \int \frac{n(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d\mathbf{x}' + v_{xc}(\mathbf{x}),$$

where the exchange-correlation potential $v_{xc}(\mathbf{x})$ is defined as,

$$v_{xc}(\mathbf{x}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{x})}.$$

4. Repeat from step 2 until self-consistency is achieved.

In LDA the exchange-correlation functional is an explicit functional of electron density $n(\mathbf{x})$, and the exchange-correlation potential $v_{xc}(\mathbf{x})$ can be obtained by straightforward differentiation. In the case of the diagrammatic expansion, this simple property no longer holds and $E_{xc}[n]$ appears as an implicit functional of $n(\mathbf{x})$. The exchange-correlation potential $v_{xc}(\mathbf{x})$ can still be found using the equation:

$$v_{xc}(\mathbf{x}) = - \int \mathcal{D}(\mathbf{x}, \mathbf{x}') \frac{\delta E_{xc}[n]}{\delta J_0(\mathbf{x}')} d\mathbf{x}',$$

The functional derivative in the above expression can be easily evaluated based on the following relationships:

$$\frac{\delta \mathcal{G}_0(x_1, x_2)}{\delta J_0(\mathbf{x})} = \int_0^\beta \mathcal{G}_0(x_1, x) \mathcal{G}_0(x, x_2) d\tau,$$

$$\frac{\delta \mathcal{D}(\mathbf{x}, \mathbf{x}')}{\delta \mathcal{G}_0(x_1, x_2)} = 2\mathcal{D}(\mathbf{x}, \mathbf{x}_1) \mathcal{G}_0(x_1, x_2) \mathcal{D}(\mathbf{x}_2, \mathbf{x}').$$

For example, the first order correction to $v_{xc}(\mathbf{x})$ is given by,

$$v_{xc,1}(\mathbf{x}) = \frac{1}{\beta}$$

Obviously, even in case of the diagrammatic expansion of E_{xc} one could still use the above mentioned self-consistent procedure. To reduce the computational effort, however, slight modification of that procedure might be advantageous. Namely, we suggest to shift the emphasis from density n to Kohn-Sham potential J_0 . Indeed, Corollary 1 guarantees that there is a one-to-one correspondence between n and J_0 . Thus, we can consider the effective action functional that depends on J_0 rather than n :

$$\overline{\Gamma}[J_0] \equiv \Gamma[n[J_0]].$$

The variational principle then takes the form

$$\frac{\delta \bar{\Gamma}[J_0]}{\delta J_0(\mathbf{x})} = 0.$$

In other words, one has to find a Kohn-Sham potential that minimizes the effective action functional $\bar{\Gamma}[J_0]$. To accomplish this task, one could use the so-called steepest descent minimization method.²⁷ In this case the self-consistent procedure takes the form:

1. Start with some reasonable guess for the Kohn-Sham potential $J_0(\mathbf{x})$.
2. Calculate the direction of steepest descent $s(\mathbf{x})$ as,

$$s(\mathbf{x}) = -\frac{\delta\bar{\Gamma}[J_0]}{\delta J_0(\mathbf{x})}$$

or

$$s(\mathbf{x}) = -\int \mathcal{D}^{-1}(\mathbf{x}, \mathbf{x}') J_0(\mathbf{x}') d\mathbf{x}' - \frac{\delta\bar{\Gamma}_{int}[J_0]}{\delta J_0(\mathbf{x})}$$

3. Determine new Kohn-Sham potential $J_0^{new}(\mathbf{x})$ from the old Kohn-Sham potential $J_0^{old}(\mathbf{x})$ by stepping along the direction of steepest descent:

$$J_0^{new}(\mathbf{x}) = J_0^{old}(\mathbf{x}) + \alpha s(\mathbf{x})$$

where α is the length of the step.

4. Repeat from step 2 until self-consistency is achieved.

The advantage of this self-consistent procedure is that it is much easier to calculate

$$\frac{\delta\bar{\Gamma}[J_0]}{\delta J_0(\mathbf{x})}$$

rather than

$$\frac{\delta\Gamma[n]}{\delta n(\mathbf{x})}.$$

For example, when $\bar{\Gamma}_{int}[J_0]$ is approximated by its first order correction

$$\bar{\Gamma}_{int}[J_0] \approx \frac{1}{2\beta} \text{---} \text{---} \text{---} - \frac{1}{2\beta} \text{---} \text{---} \text{---}$$

the steepest descent direction is given by

$$s(\mathbf{x}) = -\int \mathcal{D}^{-1}(\mathbf{x}, \mathbf{x}') \left(J_0(\mathbf{x}') - \int \frac{n(\mathbf{x}'')}{|\mathbf{x}'' - \mathbf{x}'|} d\mathbf{x}'' \right) d\mathbf{x}' + \int_0^\beta d\tau \int \int \mathcal{G}_0(\mathbf{y}0, \mathbf{x}\tau) \mathcal{G}_0(\mathbf{x}\tau, \mathbf{y}'0) \frac{n(\mathbf{y}', \mathbf{y})}{|\mathbf{y}' - \mathbf{y}|} d\mathbf{y} d\mathbf{y}'.$$

The advantage of this expression as compared to the first order correction to $v_{xc,1}$ is that here, we avoid the calculation of the inverse density propagator $\mathcal{D}(\mathbf{x}, \mathbf{x}')$. Note that $\mathcal{D}^{-1}(\mathbf{x}, \mathbf{x}')$ can easily be written in terms of Kohn-Sham single-particle orbitals and energies (see Eqn (28)).

V. TIME-DEPENDENT PROBE

To study excitation energies and one-electron propagators, it is necessary to consider an imaginary-time-dependent probe. The definition of the functional $W[J]$ is changed correspondingly

$$e^{-W[J]} = \int D\psi^\dagger D\psi e^{-S[\psi^\dagger, \psi] - \int J(x)\psi^\dagger(x)\psi(x)dx}. \quad (29)$$

Note that the parameter β has been absorbed into $W[J]$. In order to proceed with the inversion method, we need to assure that the map $J(x) \rightarrow n(x)$,

$$n(x) = \frac{\delta W[J]}{\delta J(x)}, \quad (30)$$

is invertible. Since at the end the time-dependent probe is set to zero, we can assume our source to be infinitesimally small. Therefore it suffices to prove the invertibility in the small neighborhood of *time-independent* external source:

$$J(\mathbf{x}) + \delta J(x) \rightarrow n(\mathbf{x}) + \delta n(x).$$

Since,

$$\delta n(x) = \int \left(\frac{\delta^2 W[J]}{\delta J(x) \delta J(x')} \right)_{J(\mathbf{x})} \delta J(x') dx',$$

we need to show that the operator

$$W^{(2)}(x, x') \equiv \left(\frac{\delta^2 W[J]}{\delta J(x) \delta J(x')} \right)_{J(\mathbf{x})}$$

has no zero eigenvalues. This property follows from the following theorem.

Theorem 2: *The operator $W^{(2)}(x, x')$ is strictly negative definite.* (The proof is given in the appendix.)

This theorem guarantees that as long as two infinitesimally small probes differ by more than a pure time-dependent function, they would produce two different densities. Once this one-to-one correspondence has been established, further analysis proceeds similar to the time-independent case. The effective action functional is defined as,

$$\Gamma[n] = W[J] - \int J(x) n(x) dx,$$

where J is assumed to be a functional of n by Eqn (30). Using the inversion method,¹¹ the effective action functional can be found as a power series in terms of the coupling constant:

$$\Gamma[n, e^2] = \Gamma_0[n] + e^2 \Gamma_1[n] + e^4 \Gamma_2[n] + \dots$$

Zeroth order term is given by,

$$\Gamma_0[n] = W_0[J_0] - \int J_0(x) n(x) dx.$$

The functional $W_0[J_0]$ describes a Kohn-Sham system of noninteracting electrons in the presence of an imaginary-time-dependent external potential $J_0(x)$. Kohn-Sham potential $J_0(x)$ is chosen such that the time-dependent density $n(x)$ is reproduced. Diagrammatic structure of $\Gamma_i[n]$ is the same as its time-independent counterparts with the only difference being that Kohn-Sham propagator is now defined in the presence of a time-dependent Kohn-Sham potential $J_0(x)$,

$$\mathcal{G}_0^{-1}(x, x') = - \left(\frac{\partial}{\partial \tau} - \frac{\nabla^2}{2m} + v_{ion}(\mathbf{x}) + J_0(x) \right) \delta(x - x'),$$

and the inverse density propagator becomes

$$\mathcal{D}(x, x') = - [\mathcal{G}_0(x, x') \mathcal{G}_0(x', x)]^{-1}.$$

VI. ONE-ELECTRON PROPAGATORS

Using the effective action formalism it is possible to develop a systematic Kohn-Sham density-functional approach to one-electron propagators. It is common practice to use converged Kohn-Sham single-particle orbitals and energies in quasiparticle calculations. However, very often these methods are not very systematic in their use of Kohn-Sham based quantities.¹⁷ The formalism presented below provides a rigorous theoretical foundation for the calculation of quasiparticle properties based on Kohn-Sham noninteracting system.

Consider $W[J]$ in the presence of the auxiliary nonlocal source $\xi(x, x')$

$$e^{-W[J]} = \int D\psi^\dagger D\psi e^{-S_\xi[\psi^\dagger, \psi]},$$

where

$$\begin{aligned} S_\xi[\psi^\dagger, \psi] &= S[\psi^\dagger, \psi] + \int J(x) \psi^\dagger(x) \psi(x) dx \\ &+ \int \int \xi(x, x') \psi^\dagger(x) \psi(x') dx dx'. \end{aligned}$$

The nonlocal source, $\xi(x, x')$, allows us to write the one-electron propagator or the (finite temperature) Green's function, $\mathcal{G}(x, x') = -\langle T_\tau \psi(x) \psi^\dagger(x') \rangle$, as a functional derivative

$$\mathcal{G}(x, x') = \left(\frac{\delta W[J]}{\delta \xi(x', x)} \right)_J.$$

Using the well-known property of the Legendre transformation,²⁸

$$\left(\frac{\delta W[J]}{\delta \xi(x', x)} \right)_J = \left(\frac{\delta \Gamma[n]}{\delta \xi(x', x)} \right)_n, \quad (31)$$

the one-electron propagator can be expressed in terms of the effective action functional as,

$$\mathcal{G}(x, x') = \left(\frac{\delta \Gamma_0[n]}{\delta \xi(x', x)} \right)_n + \left(\frac{\delta \Gamma_{int}[n]}{\delta \xi(x', x)} \right)_n. \quad (32)$$

Using the property (31) we obtain that

$$\left(\frac{\delta \Gamma_0[n]}{\delta \xi(x', x)} \right)_n = \left(\frac{\delta W_0[J_0]}{\delta \xi(x', x)} \right)_{J_0} = \mathcal{G}_0(x, x'). \quad (33)$$

Let us consider the second term in Eqn (32). One can show that

$$\begin{aligned} \left(\frac{\delta \Gamma_{int}[n]}{\delta \xi(x', x)} \right)_n &= \int \int \frac{\delta \Gamma_{int}[n]}{\delta \mathcal{G}_0(y, y')} \mathcal{G}_0(y, x') \mathcal{G}_0(x, y') dy dy' \\ &- \int \frac{\delta \Gamma_{int}[n]}{\delta n(y)} \mathcal{G}_0(y, x') \mathcal{G}_0(x, y) dy. \end{aligned} \quad (34)$$

Our original system is recovered by setting ξ to zero. Using Eqns (32), (33), (34) the exact one-electron propagator (in operator notation) is given by,

$$\mathcal{G} = \mathcal{G}_0 + \mathcal{G}_0 \cdot \Sigma_0 \cdot \mathcal{G}_0, \quad (35)$$

where the Kohn-Sham self-energy Σ_0 is given by,

$$\Sigma_0(x_1, x_2) = \frac{\delta \Gamma_{int}[n]}{\delta \mathcal{G}_0(x_2, x_1)} - J_0(x_1) \delta(x_1 - x_2) \quad (36)$$

and $J_0(x_1)$ is the Kohn-Sham potential,

$$J_0(x) = \frac{\delta \Gamma_{int}[n]}{\delta n(x)}.$$

The functional derivative in Eqn (36) can be easily evaluated since the functional Γ_{int} can be expressed entirely in terms of Kohn-Sham Green's functions \mathcal{G}_0 . The above expression for the one-electron propagator can also be written as,

$$\mathcal{G} = \mathcal{G}_0 + \mathcal{G}_0 \cdot \tilde{\Sigma}_0 \cdot \mathcal{G},$$

where

$$\tilde{\Sigma}_0 = \Sigma_0 \cdot (1 + \mathcal{G}_0 \cdot \Sigma_0)^{-1} = (\Sigma_0^{-1} + \mathcal{G}_0)^{-1}.$$

Therefore the exact self-energy Σ is given by,

$$\Sigma(x, x') = J_0(x)\delta(x - x') + \tilde{\Sigma}_0(x, x').$$

The above formulation provides a systematic way to study one-electron propagators and self-energy in Kohn-Sham density-functional theory. The important feature of this formulation is that both self-energy and Kohn-Sham potential are determined from one quantity $\Gamma_{int}[n]$. *A single approximation to the functional $\Gamma_{int}[n]$ simultaneously generates both the self-energy and Kohn-Sham potential.* This is to be contrasted with the common strategy of performing *separate* approximations for Kohn-Sham potential and the self-energy.¹⁷

VII. EXCITATION ENERGIES

In addition to one-electron propagators, the effective action formalism allows a systematic study of the many-body excited states in density-functional theory.⁴ Consider the Fourier transform of $W^{(2)}(x, x')$:

$$W^{(2)}(\mathbf{x}, \mathbf{x}', i\nu_s) = \int_0^\beta W^{(2)}(x, x') e^{i\nu_s(\tau - \tau')} d(\tau - \tau'),$$

$$\nu_s = 2\pi s/\beta,$$

It can be analytically continued into the complex plane ω :

$$W^{(2)}(\mathbf{x}, \mathbf{x}', \omega) = W^{(2)}(\mathbf{x}, \mathbf{x}', i\nu_s) \big|_{i\nu_s \rightarrow \omega + i\eta}.$$

The proposition below guarantees that this analytic continuation has an inverse in the upper complex plane ω including the real axis.

Proposition 2: *The operator $W^{(2)}(\mathbf{x}, \mathbf{x}', \omega)$ has no zero eigenvalues when ω is located in the upper half of the complex plane including the real axis. (see appendix for the proof.)*

Let us define the excitation kernel as,

$$\Gamma^{(2)}(x, x') = \left(\frac{\delta \Gamma^2[n]}{\delta n(x) \delta n(x')} \right)_{n(\mathbf{x})}.$$

It easy to show that

$$\int W^{(2)}(x, x') \Gamma^{(2)}(x', y) dx' = -\delta(x - y),$$

or in terms of Fourier transforms

$$\int W^{(2)}(\mathbf{x}, \mathbf{x}', i\nu_s) \Gamma^{(2)}(\mathbf{x}', \mathbf{y}, -i\nu_s) d\mathbf{x}' = -\delta(\mathbf{x} - \mathbf{y}). \quad (37)$$

Proposition 3: $\Gamma^{(2)}(\mathbf{x}, \mathbf{y}, -i\nu_s)$ has a unique analytic continuation $\Gamma^{(2)}(\mathbf{x}, \mathbf{y}, -\omega)$ such that

1. it does not have any zeros in the upper half of the complex plane ω including the real axis.
2. $[\Gamma^{(2)}(\mathbf{x}, \mathbf{y}, -\omega)]^{-1} \sim \frac{1}{|\omega|}, (\omega \rightarrow \infty).$

The proof is given in the appendix. Based on the above statement we can extend the relationship (37) to the whole complex plane ω :

$$\int W^{(2)}(\mathbf{x}, \mathbf{x}', \omega) \Gamma^{(2)}(\mathbf{x}', \mathbf{y}, -\omega) d\mathbf{x}' = -\delta(\mathbf{x} - \mathbf{y}). \quad (38)$$

Consider $W^{(2)}(\mathbf{x}, \mathbf{x}', \omega)$ in the zero temperature limit ($\beta \rightarrow \infty$). It is well-known that it has poles just below the real axis at the exact excitation energies,

$$\omega = E_l - E_0 - i\eta.$$

Then it follows from Eqn (38) that $\Gamma^{(2)}(\mathbf{x}, \mathbf{y}, -\omega)$ has zero eigenvalues at the exact excitation energies.⁴ In other words, when $\omega = E_l - E_0 - i\eta$, there exists $\xi(\mathbf{x})$ such that,⁴

$$\int \Gamma^{(2)}(\mathbf{x}, \mathbf{y}, -\omega) \xi(\mathbf{x}) d\mathbf{x} = 0. \quad (39)$$

Using the coupling constant expansion for $\Gamma(n)$ the excitation kernel becomes

$$\Gamma^{(2)}(\mathbf{x}, \mathbf{y}, -i\nu_s) = \Gamma_0^{(2)}(\mathbf{x}, \mathbf{y}, -i\nu_s) + \Gamma_{int}^{(2)}(\mathbf{x}, \mathbf{y}, -i\nu_s).$$

Substituting this in Eqn (39) and using the fact that,

$$\left[\Gamma_0^{(2)}(\mathbf{x}, \mathbf{x}', -\omega) \right]^{-1} = -W_0^{(2)}(\mathbf{x}, \mathbf{x}', \omega),$$

we obtain

$$\xi(\mathbf{x}) = \int \int W_0^{(2)}(\mathbf{x}, \mathbf{x}', \omega) \Gamma_{int}^{(2)}(\mathbf{x}', \mathbf{y}', -\omega) \xi(\mathbf{y}') d\mathbf{x}' d\mathbf{y}'. \quad (40)$$

Here $W_0^{(2)}(\mathbf{x}, \mathbf{x}', \omega)$ represents the negative of the density-correlation function for Kohn-Sham noninteracting system;

$$W_0^{(2)}(\mathbf{x}, \mathbf{x}', \omega) = \sum_l \frac{n_l^*(\mathbf{x}) n_l(\mathbf{x}')}{\omega - \omega_l^{ks} + i\eta} - \frac{n_l(\mathbf{x}) n_l^*(\mathbf{x}')}{\omega + \omega_l^{ks} + i\eta},$$

where

$$\langle l^{ks} | \hat{n}(\mathbf{x}) | 0^{ks} \rangle = n_l(\mathbf{x}),$$

and

$$\omega_l^{ks} = E_l^{ks} - E_0^{ks}.$$

Here all the quantities refer to the Kohn-Sham noninteracting system. Aside from the notational differences, Eqn (40) coincides with similar expressions derived using time-dependent DFT.^{18,19} Searching for a solution of the form

$$\xi(\mathbf{x}) = \sum a_l n_l(\mathbf{x}) + \sum b_l n_l^*(\mathbf{x}),$$

we obtain the following matrix equation,¹⁹

$$\begin{bmatrix} L & M \\ M^* & L^* \end{bmatrix} \begin{bmatrix} A \\ B \end{bmatrix} = (\omega + i\eta) \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} A \\ B \end{bmatrix},$$

where

$$M_{ij} = \int \int n_i^*(\mathbf{x}) \Gamma_{int}^{(2)}(\mathbf{x}, \mathbf{y}, -\omega) n_j^*(\mathbf{y}) d\mathbf{x} d\mathbf{y},$$

$$L_{ij} = \int \int n_i^*(\mathbf{x}) \Gamma_{int}^{(2)}(\mathbf{x}, \mathbf{y}, -\omega) n_j(\mathbf{y}) d\mathbf{x} d\mathbf{y} \\ + (E_i - E_0) \delta_{ij},$$

and

$$(A)_i = a_i, (B)_i = b_i.$$

The values of ω for which the above matrix equation has nontrivial solutions, is determined by the condition

$$\det \left(\begin{bmatrix} L & M \\ M^* & L^* \end{bmatrix} - (\omega + i\eta) \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \right) = 0.$$

Therefore, the effective action formalism presents an alternative way (as compared to time-dependent density-functional theory) for calculating the excitation energies. However, in addition to it, the effective action formalism also provides a means of calculating the exchange-correlation kernel. This feature is missing in conventional time-dependent density-functional theory.²⁰

VIII. CONCLUDING REMARKS.

Based on the effective action formalism⁴ we developed a rigorous formulation of generalized Kohn-Sham theory. This formulation is specifically geared towards practical calculations of the ground and excited properties of real systems. Indeed, in the case of a particle-density based description of nonrelativistic many-electron system we arrived at a systematic way to study the exchange-correlation functional, one-electron propagators and many-body excitation energies entirely in terms Kohn-Sham single-particle orbitals and energies. The presented formalism is very general and can be applied to a various many-body systems for constructing Kohn-Sham like description in terms of the expectation value of any general operator (e.g. spin-density, current-density-functional theory).

IX. ACKNOWLEDGMENTS.

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APPENDIX A: PROPERTIES OF FUNCTIONALS $W[J]$ AND $\Gamma[Q]$.

1. Time-independent probe

Theorem 1: *The functional $W[J] = -\frac{1}{\beta} \ln \text{Tr} \left(e^{-\beta(\hat{H} + J(1)\hat{Q}(1))} \right)$ is strictly concave, i.e. for any α , $0 < \alpha < 1$, and $J \neq J'$*

$$W[\alpha J + (1 - \alpha) J'] > \alpha W[J] + (1 - \alpha) W[J']$$

Proof:²⁹

Consider two Hermitian operators \hat{A} and \hat{B} . Let $\{\Psi_i\}$ be a complete set of eigenstates of the operator $\alpha\hat{A} + (1 - \alpha)\hat{B}$. Then

$$\begin{aligned} \text{Tr} \left(e^{\alpha\hat{A} + (1-\alpha)\hat{B}} \right) &= \sum_i \left\langle \Psi_i \left| e^{\alpha\hat{A} + (1-\alpha)\hat{B}} \right| \Psi_i \right\rangle \\ &= \sum_i e^{\alpha\langle \Psi_i | \hat{A} | \Psi_i \rangle + (1-\alpha)\langle \Psi_i | \hat{B} | \Psi_i \rangle}. \end{aligned}$$

Using Hölder's inequality³⁰ ($a_i, b_i \geq 0$),

$$\sum_i a_i^\alpha b_i^{1-\alpha} \leq \left(\sum_i a_i \right)^\alpha \left(\sum_i b_i \right)^{1-\alpha},$$

we obtain that

$$\text{Tr} \left(e^{\alpha\hat{A} + (1-\alpha)\hat{B}} \right) \leq \left(\sum_i e^{\langle \Psi_i | \hat{A} | \Psi_i \rangle} \right)^\alpha \left(\sum_i e^{\langle \Psi_i | \hat{B} | \Psi_i \rangle} \right)^{(1-\alpha)}$$

From Hölder's inequality it follows that the equality in the above expression holds only if for any i

$$\left\langle \Psi_i \left| \hat{A} \right| \Psi_i \right\rangle = \left\langle \Psi_i \left| \hat{B} \right| \Psi_i \right\rangle + \chi, \tag{A1}$$

where χ is constant independent of i .

Since e^x is a convex function,

$$\begin{aligned} \sum_i e^{\langle \Psi_i | \hat{A} | \Psi_i \rangle} &\leq \sum_i \left\langle \Psi_i \left| e^{\hat{A}} \right| \Psi_i \right\rangle, \\ \sum_i e^{\langle \Psi_i | \hat{B} | \Psi_i \rangle} &\leq \sum_i \left\langle \Psi_i \left| e^{\hat{B}} \right| \Psi_i \right\rangle. \end{aligned} \tag{A2}$$

Equal sign in the above equations holds only if $\{\Psi_i\}$ are the eigenstates \hat{A} and \hat{B} . Collecting all the results together we obtain the following inequality:

$$\text{Tr} \left(e^{\alpha \hat{A} + (1-\alpha) \hat{B}} \right) \leq \left(\text{Tr} e^{\hat{A}} \right)^\alpha \left(\text{Tr} e^{\hat{B}} \right)^{(1-\alpha)}. \quad (\text{A3})$$

Equality holds here if and only if operators \hat{A} and \hat{B} differ by a constant:

$$\hat{A} = \hat{B} + \text{const.} \quad (\text{A4})$$

Indeed:

\Rightarrow) Suppose Eqn A4 is true, then equal sign in (A3) is obvious.

\Leftarrow) If there is an equal sign in (A3) then operators \hat{A} and \hat{B} must have a common set of eigenstates $\{\Psi_i\}$ and condition (A1) must be true. Then considering the representation of operators \hat{A} and \hat{B} in the basis of eigenfunctions $\{\Psi_i\}$ we obtain

$$\hat{A} = \hat{B} + \text{const.}$$

Therefore

$$\text{Tr} \left(e^{\alpha \hat{A} + (1-\alpha) \hat{B}} \right) < \left(\text{Tr} e^{\hat{A}} \right)^\alpha \left(\text{Tr} e^{\hat{B}} \right)^{(1-\alpha)},$$

when $\hat{A} \neq \hat{B} + \text{const.}$

Setting

$$\hat{A} = -\beta \left(\hat{H} + J(1) \hat{Q}(1) \right)$$

and

$$\hat{B} = -\beta \left(\hat{H} + J'(1) \hat{Q}(1) \right),$$

we can easily obtain

$$W[\alpha J + (1-\alpha) J'] > \alpha W[J] + (1-\alpha) W[J'],$$

when $J \neq J'$. *QED.*

Corollary 1: *The map $\mathcal{J} \rightarrow \mathcal{Q}$ is one-to-one.*

Proof: Consider the functional

$$\Lambda[J] = W[J] - J(1') Q(1'),$$

where J and Q are considered to be independent. Since $W[J]$ is strictly concave (Theorem 1), it follows that $\Lambda[J]$ is strictly concave. Therefore if $\Lambda[J]$ has an extremum it is unique. Hence if the equation

$$\frac{\delta \Lambda[J]}{\delta J(1)} = \frac{\delta W[J]}{\delta J(1)} - Q(1) = 0$$

has a solution, it is unique. *QED.*

Proposition 1: *The effective action functional $\Gamma[Q]$ defined on the set \mathcal{Q} is strictly convex.*

Proof: Consider the family of the functionals $\{\Lambda[J, Q] : J \in \mathcal{J}, Q \in \mathcal{Q}\}$,

$$\Lambda[J, Q] = W[J] - J(1') Q(1').$$

Here Q is considered to be independent of J . Obviously $\Lambda[J, Q]$ is linear in Q . The effective action functional can be defined as

$$\Gamma[Q] = \sup \{ \Lambda[J, Q], J \in \mathcal{J} \}. \quad (\text{A5})$$

The above expression represents the most general way to define the effective action functional. In our case two definitions, Eqn (6) and Eqn (A5), are equivalent. Convexity of $\Gamma[Q]$ follows from the fact that it is a supremum of the family of the linear functionals (in Q). Because by construction for any element $J \in \mathcal{J}$, there corresponds only one $Q \in \mathcal{Q}$, the functional $\Gamma[Q]$ is also strictly convex. *QED.*

2. Time-dependent probe

Theorem 2: *The operator $W^{(2)}(x, x')$ is strictly negative definite*

Proof: We have to prove that there exists no function $f(\mathbf{x}, \tau) \neq \eta(\tau)$ such that

$$\int \int f^*(x) W^{(2)}(x, x') f(x') dx dx' \geq 0. \quad (\text{A6})$$

The operator $W^{(2)}(x, x')$ actually represents the negative of the density correlation function in the presence of the *time-independent* source $J(\mathbf{x})$:

$$W^{(2)}(x, x') = - \frac{\int D\psi^\dagger D\psi \tilde{n}(x) \tilde{n}(x') e^{-S_J[\psi^\dagger, \psi]}}{\int D\psi^\dagger D\psi e^{-S_J[\psi^\dagger, \psi]}},$$

where

$$S_J[\psi^\dagger, \psi] = S[\psi^\dagger, \psi] + \int J(\mathbf{x}) n(x) dx,$$

and $\tilde{n}(x)$ denotes density fluctuation operator,

$$\tilde{n}(x) = \psi^\dagger(x) \psi(x) - n(x).$$

Defining a Fourier transform as,

$$W^{(2)}(\mathbf{x}, \mathbf{x}', i\nu_s) = \int_0^\beta W^{(2)}(x, x') e^{i\nu_s(\tau - \tau')} d(\tau - \tau'),$$

$$\nu_s = 2\pi s / \beta,$$

left hand side of (A6) transforms into

$$\sum_{\nu_s} \int \int (f(\mathbf{x}, \nu_s))^* W^{(2)}(\mathbf{x}, \mathbf{x}', i\nu_s) f(\mathbf{x}', \nu_s) d\mathbf{x} d\mathbf{x}'. \quad (\text{A7})$$

Strict concavity of $W[J]$ for time-independent case guarantees that $\nu_s = 0$ term is strictly negative definite. For convenience, we ignore this term from the sum. Lehman representation for $W^{(2)}(\mathbf{x}, \mathbf{x}', i\nu_s)$ is given by,

$$W^{(2)}(\mathbf{x}, \mathbf{x}', i\nu_s) = e^{W[J]} \sum_{ml} \frac{e^{-\beta E_m} - e^{-\beta E_l}}{E_m - E_l + i\nu_s} \times$$

$$\times \langle m | \tilde{n}(\mathbf{x}) | l \rangle \langle l | \tilde{n}(\mathbf{x}') | m \rangle, \quad (\text{A8})$$

where

$$\left(\hat{H} + \int J(\mathbf{x}) \hat{n}(\mathbf{x}) \right) |m\rangle = E_m |m\rangle,$$

$$\left(\hat{H} + \int J(\mathbf{x}) \hat{n}(\mathbf{x}) \right) |l\rangle = E_l |l\rangle.$$

Therefore an arbitrary ($\nu_s \neq 0$) term in the sum (A7) can be written as,

$$e^{W[J]} \sum_{ml} \frac{e^{-\beta E_m} - e^{-\beta E_l}}{E_m - E_l + i\nu_s} \left| \left\langle m \left| \int \tilde{n}(\mathbf{x}) f(\mathbf{x}, \nu_s) d\mathbf{x} \right| l \right\rangle \right|^2,$$

or

$$e^{W[J]} \sum_{E_m < E_l} \left| \left\langle m \left| \int \tilde{n}(\mathbf{x}) f(\mathbf{x}, \nu_s) d\mathbf{x} \right| l \right\rangle \right|^2 \times$$

$$\times \left(\frac{e^{-\beta E_m} - e^{-\beta E_l}}{E_m - E_l + i\nu_s} + \frac{e^{-\beta E_l} - e^{-\beta E_m}}{E_l - E_m + i\nu_s} \right).$$

After a simple algebra we obtain

$$e^{W[J]} \sum_{E_m < E_l} 2 \left| \left\langle m \left| \int \tilde{n}(\mathbf{x}) f(\mathbf{x}, \nu_s) d\mathbf{x} \right| l \right\rangle \right|^2 \times \\ \times \frac{e^{-\beta E_l} - e^{-\beta E_m}}{(E_l - E_m)^2 + \nu_s^2} (E_l - E_m).$$

Obviously, the above expression cannot be positive. Moreover, it cannot be zero since this would imply that for all $m \neq l$

$$\left\langle m \left| \int \hat{n}(\mathbf{x}) f(\mathbf{x}, \nu_s) d\mathbf{x} \right| l \right\rangle = 0$$

and $\int \hat{n}(\mathbf{x}) f(\mathbf{x}, \nu_s) d\mathbf{x}$ commutes with the Hamiltonian. This is impossible unless $f(\mathbf{x}, \nu_s)$ is constant independent of \mathbf{x} or $f(\mathbf{x}, \tau)$ is a function of τ only. This case, however, was excluded from the very beginning. Therefore, the operator $W^{(2)}(x, x')$ is strictly negative definite. *QED.*

Proposition 2: *The operator $W^{(2)}(\mathbf{x}, \mathbf{x}', \omega) = W^{(2)}(\mathbf{x}, \mathbf{x}', i\nu_s) |_{i\nu_s \rightarrow \omega + i\eta}$ has no zero eigenvalues when ω is located in the upper half of the complex plane including the real axis.*

Proof: Suppose $f(\mathbf{x})$ is an eigenvector corresponding to a zero eigenvalue then

$$\int \int f^*(\mathbf{x}) W^{(2)}(\mathbf{x}, \mathbf{x}', \omega) f(\mathbf{x}') d\mathbf{x} d\mathbf{x}' = 0. \quad (\text{A9})$$

Using Lehman representation we obtain

$$0 = \sum_{E_m < E_l} \left| \left\langle m \left| \int \tilde{n}(\mathbf{x}) f(\mathbf{x}) d\mathbf{x} \right| l \right\rangle \right|^2 \times \\ \times \left(\frac{e^{-\beta E_m} - e^{-\beta E_l}}{z - (E_l - E_m)} - \frac{e^{-\beta E_m} - e^{-\beta E_l}}{z + (E_l - E_m)} \right)$$

where $z = \omega + i\eta$. Consider the imaginary part of the above expression,

$$0 = -4 \operatorname{Re}(z) \operatorname{Im}(z) \sum_{E_m < E_l} \left| \left\langle m \left| \int \tilde{n}(\mathbf{x}) f(\mathbf{x}) d\mathbf{x} \right| l \right\rangle \right|^2 \times \\ \times \frac{(E_l - E_m) (e^{-\beta E_m} - e^{-\beta E_l})}{|z^2 - (E_l - E_m)^2|^2} \\ \Rightarrow \operatorname{Re}(z) \operatorname{Im}(z) = 0.$$

By Theorem 2, the real part of z cannot be zero, since in this case $W^{(2)}(\mathbf{x}, \mathbf{x}', \omega = i\nu_s)$ is strictly negative definite and condition (A9) cannot be satisfied. Therefore we necessarily obtain that $\operatorname{Im}(z) = 0$ and

$$\omega + i\eta = \text{real} \quad \Rightarrow \quad \omega = \text{real} - i\eta$$

Therefore $W^{(2)}(\mathbf{x}, \mathbf{x}', \omega)$ may have zero eigenvalues only when ω is located in the lower half of the complex plane excluding the real axis. *QED.*

Proposition 3: $\Gamma^{(2)}(\mathbf{x}, \mathbf{y}, -i\nu_s)$ has a unique analytic continuation $\Gamma^{(2)}(\mathbf{x}, \mathbf{y}, \omega)$ such that

1. it does not have any zeros in the upper half of the complex plane ω including the real axis
2. $[\Gamma^{(2)}(\mathbf{x}, \mathbf{y}, \omega)]^{-1} \sim \frac{1}{|\omega|}, (\omega \rightarrow \infty).$

Proof:

Existence follows from the fact that $\Gamma^{(2)}(\mathbf{x}, \mathbf{y}, \omega)$ can be defined as $-[W^{(2)}(\mathbf{x}, \mathbf{y}, \omega)]^{-1}$. Suppose there exist two analytic continuations of $\Gamma^{(2)}(\mathbf{x}, \mathbf{y}, -i\nu_s)$ with the properties 1 and 2. Then $W^{(2)}(\mathbf{x}, \mathbf{x}', i\nu_s)$ will have two different analytic continuations which is impossible. *QED.*

- ¹ P. Hohenberg and W. Kohn, Phys. Rev. **136B**, 864(1964).
- ² U. von Barth, L. Hedin, J. Phys. C**5**, 1629(1972); M. M. Pant, A. K. Rajagopal, Sol. State Comm., **10**, 1157(1972).
- ³ G. Vignale, M. Rasolt, Phys. Rev. Lett., **59**, 2360(1987).
- ⁴ R. Fukuda, T. Kotani, and S. Yokojima, Prog. Theor. Phys. **92**, 833(1994).
- ⁵ R. Fukuda, M. Komachiya, S. Yokojima, Y. Suzuki, K. Okumura and T. Inagaki, Prog. Theor. Phys. Suppl. **121**, (1995).
- ⁶ N. D. Mermin, Phys. Rev., **137**, A1414(1965).
- ⁷ W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133(1965).
- ⁸ P. C. Hohenberg, W. Kohn, L.J. Sham, Adv. Quant. Chem. **21**, 7(1990).
- ⁹ R. M. Dreizler, E. K. U. Gross, *Density-Functional Theory*, (Springer-Verlag, Berlin, Heidelberg, 1990) and references therein.
- ¹⁰ R. G. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*, (Oxford University Press, New York, 1989).
- ¹¹ K. Okumura, Int. J. Mod. Phys. **11**, 65(1996).
- ¹² L. J. Sham, Phys. Rev. **B32**, 3876(1985).
- ¹³ J. B. Krieger and Yan Li, G. J. Iafrate, Phys. Rev. **A45**, 101(1992).
- ¹⁴ M. Valiev and G. W. Fernando, Phys. Lett. A **227**, 265(1997).
- ¹⁵ L. J. Sham and W. Kohn, Phys. Rev. **145**, 561(1966).
- ¹⁶ M. Schlüter, L.J. Sham, Adv. Quant. Chem. **21**, 97(1990), and references therein.
- ¹⁷ R. Del Sole, L. Reining, R. W. Godby, Phys. Rev. **B49**, 8024(1994), and references therein.
- ¹⁸ M. Petersilka, U.J. Gossmann, E.K.U. Gross, Phys. Rev. Lett. **76**, 1212(1996).
- ¹⁹ R. Bauernschmitt, R. Ahlrichs, Chem. Phys. Lett. **256**, 454(1996).
- ²⁰ E. K. U. Gross, W. Kohn, Adv. Quant. Chem. **21**, 255(1990).
- ²¹ the usefulness of the Legendre transformation in density-functional theory was earlier recognized by E.H. Lieb in *Density Functional Methods in Physics*, edited by R.M. Dreizler and J. da Providencia (Plenum Press, New York, 1985); and Nalewajski, J. Chem. Phys. **78**, 6112(1983) and references therein.
- ²² M. Valiev and G. W. Fernando, Phys. Rev. **B54**, 7765(1996).
- ²³ J. W. Negele and H. Orland, *Quantum Many-Particle Systems*, (Addison-Wesley, 1995).
- ²⁴ A. Görling, M. Levy, Phys. Rev. **B47**, 13105(1993).
- ²⁵ A. Görling, M. Levy, Phys. Rev. **A50**, 196(1994).
- ²⁶ L. H. Ryder, *Quantum Field Theory* (Cambridge University Press, New York, 1985).
- ²⁷ S. S. Rao, *Optimization theory and applications*, (Halsted Press, New York, 1978).
- ²⁸ J. Zinn-Justin, *Quantum Field Theory and Critical Phenomena*, (Clarendon Press, Oxford, 1993).
- ²⁹ some of the techniques used in the proof were borrowed from R. B. Israel, *Convexity in the Theory of Lattice Gases*, (Princeton University Press, Princeton, New Jersey, 1979).
- ³⁰ A. E. Taylor, *General Theory of Functions and Integration*, (Dover Publications, Inc., New York, 1985).